Crystallisation of Spheres[1]

K. Kendall[2], C. Stainton[2], F. van Swol[3], and L. V. Woodcock[4]

2   Sandia National Laboratory, Albuquerque, NM87106, USA.

3   Department of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham,UK.

4   Department of Computational Sciences, National University of Singapore,. Singapore 119260

ABSTRACT

Simplified mathematical computer models are often used to gain insight into the way more complex real systems behave. In a notable reversion of this protocol, a colloidal suspension of sub-micron spherical particles, approximately, but not perfectly, hard and uniform were recently crystallised in space and analysed for crystal type. The objective was to establish how, and to what structure, hard spheres crystallise without the effects of gravity. Statistical thermodynamic computations indicate a freezing transition of the fluid at around 50% packing, and that the thermodynamically stable crystal phase of spheres is face centred cubic (fcc) rather than hexagonal close packed (hcp). Theory predicts an equilibrium constant between fcc and hcp of order unity. The microgravity experiments, however, resulted in a random hybrid close packed structure (rhcp) in which hexagonal layers are stacked randomly such that long range order is two dimensional. Here we report the mechanism from idealised computer "experiments" for crystallisation of thermal spheres from the metastable fluid. Model systems of up to N=64000 spheres with infinite spatial periodicity have been crystallised in runs of up to 10 billion collisions. When the fluid, initially in a metastable supercooled state at the packing fraction 58% is allowed to nucleate and freeze, a variety of structures emerge. There are three identifiable stages of structural growth: (i) initial nucleation of fcc, rhcp and also bcc-like local structures (ii) rapid growth of all incipient nucleites to random stacked 2d hexagonal (rhcp) grains, plus some fcc, to fill the volume, and (iii) relatively slow dissolution of unstable rhcp faces at grain boundaries. Finally kinetically stable nucleites emerge that are composed of hexatic layers, ordered in such a way as to contain predominantly either fcc arrangements of spheres, or rhcp, in roughly 50% proportions.

INTRODUCTION

The phase diagram of the thermodynamic hard sphere model is now well known from computer simulation. Until recently, however it was not known which of the close packed structures fcc, hcp or perhaps a hybrid or random hybrid structure is the most stable. Five different methods of computational statistical mechanics have all been recently been applied to this task. All find the fcc structure to be more stable at the freezing point than the hcp structure by a free energy difference of the order RT/1000 where R is the molar gas constant and T is absolute temperature. The question then arises, can a fluid system of hard spheres, metastable with respect to crystallisation, on time scales accessible either in nature or perhaps in computer "experiments" achieve this most stable structure and by what mechanism ?

If there were only two possibilities the answer would be simple. The free energy difference is so small that the equilibrium constant (K_p) for the transformation

$$HS_{fcc} \rightarrow HS_{hcp}$$
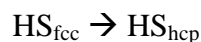
is equal to exp(-0.001) $\sim$ 1 therefore at equilibrium one expects to find a 50/50 mixture. The situation is complicated, however, because there are an infinite number of hybrid lattices and random hybrids. The completely random stacked phase has been designated rhcp. It seems likely that rhcp will be present to about 50% at equilibrium because nature cannot distinguish between hcp and rhcp. However the fcc structure is distinct due to the different lattice symmetry. The six-fold symmetry of fcc is unique.

There are two alternative empirical approaches to this problem presently available, real experiments on suspended quasi- "hard-sphere" colloids or idealised computer experiments on mathematically precise spheres. Both approaches have advantages and limitations.

In the last fifteen years a number of experimental studies have demonstrated that polymer coated colloidal particles in organic solvents bear a close resemblance to the

ideal hard sphere system. By matching the refractive indices of solvent and particle as nearly as is possible, the attractive van der Waals forces between particles can be quelled. Grafting of polymer chains to the particle surfaces ensures that the particles experience a steep repulsive interaction on close approach, never experiencing any residual van der Waals attractions. These "quasi"-hard sphere systems can serve as larger scale mimics of simpler atom-like hard sphere systems; the appeal for colloid scientists is that time scales in these systems are slow enough for experimental observation. By employing colloidal PMMA particles of diameter ~0.5 microns, sample sizes of 10^{14} cm^3 (boundary effects are likely to be negligible with such large systems) are accessible and Brownian diffusion has characteristic relaxation times typically of days. Such time scales in the colloid dimension enable the use of real time optical techniques, such as microscopy and light scattering in the study of crystal nucleation for example. As the atomic scale provides no such accessibility the results of studies on nucleation and melting become of fundamental interest.

Nevertheless, in spite of the possibility of artifacts arising from these effects, it has been demonstrated by Rutgers et al. that a colloidal system can reproduce the hard sphere equation of state *[1]*. It should be noted that interest in hard sphere crystallisation is not purely academic; SiO$_2$ nano-particles closely resemble hard spheres *[2]* and knowledge and control of their crystallisation, particularly to the fcc structure, is of significant technological use in the construction of optical switches whose operation depends crucially upon the lattice properties of the colloidal crystal *[3-4]*. Such opalescent crystals can form useful templates for inverse structures built by packing material between the interstices of the packed spheres *[5]*.

The packing of hard sphere-like particles was first examined in detail by Pusey et al. *[6]* who used light scattering studies to observe the packings of crystals produced at a number of packing fractions. They were able to produce crystals with a strong preference for fcc stacking using slow sedimentation of a fairly low packing fraction suspension with ϕ=0.25. At a slightly higher packing fraction in the coexistence region the preference for fcc stacking was less marked (with a stacking probability *[7]* of 0.58)

which was characteristic of a faster timescale for crystallisation. It was pointed out by Pusey et al. that none of the close packing simple atomic systems display such complete randomness in packing, instead choosing to be either fully fcc or hcp. This indicates perhaps, that such systems of colloidal hard spheres have not reached their equilibrium configuration, or that the influence of gravitational effects requires consideration. Indeed a number of subsequent studies have reported a slow growth in the stacking probability with time: Elliot et al. *[8]* observed structure which became more fcc-like with time looking at crystallisation from a random structure with a packing fraction of 0.529. Details of the change and its timescale were not provided. Dux and Versmold *[9]* reported the slow structural transition of a system of charge stabilised polystyrene hard sphere like particles: a nearly rhcp structure (stacking probability 0.55) was produced that was converted over a period of 40 hours to a more fcc-like structure (stacking probability 0.75). A very detailed study by Heymann et al. *[10]* looked at the crystallisation kinetics of shear-melted samples of polymer coated PMMA (polymethylmethacrylate) spheres (with packing fractions of between 0.51 and 0.57) using a light scattering method. Peaks in the scattering intensity versus wavelength plot corresponding to fcc and hcp lattices were monitored with time; they report stacking probabilities of the order of 0.9 after a long ripening stage. They also report an observation in line with the simulation findings of Courtemanche and van Swol [*11*] of heterogeneous nucleation at the walls of the suspension container on short time scales. At higher packing fractions above melting, Heymann et al. note that the induction time for homogeneous nucleation from the bulk decreases rapidly with increasing volume fraction eventually inhibiting the effects of heterogeneous nucleation. At packing fractions above the melting transition systems homogenous nucleation should be the primary method for obtaining order in the system. Experimental evidence appears to point towards fcc oriented growth of colloidal hard spheres. However all these studies include the effects of sedimentation under gravity. More recently, in an attempt to get closer to the ideal hard sphere colloidal systems by excluding the effects of gravity, similar light scattering experiments on shear-melted hard sphere suspensions were performed on board the Space Shuttle Columbia under micro-gravity [*12*]. The hard spheres used in this case were the familiar ~500 nm diameter PMMA particles with a

short (~10 nm) grafted organic layer. Packing fractions in the range between $\phi=0.5$ and $\phi=0.619$ were examined over a number of days. One of the interesting results of these experiments was that a sample with $\phi=0.537$ that showed a strong tendency to pack towards the fcc structure under gravity, showed no such tendency under microgravity. The authors report finding almost pure rhcp crystals and suggest that gravity is instrumental in converting a predominantly rhcp arrangement to fcc. They also report that microgravity enhances crystallisation: a system of particles with $\phi=0.619$ crystallised in 3.6 days; the same system, shear melted when returned to gravity, failed to crystallise over a two month period.

Zero gravity, along with the ability to achieve perfect hard spheres, is an essential feature of computer simulations. Given the surprising results from the crystallization under microgravity, the work we present here aims to use the advantages offered by computer simulation to examine the freezing kinetics of the perfect hard sphere system without the influence of gravity. In a simulation all particle coordinates can be determined for any particular moment in time; one can employ sophisticated techniques which allow one to detect structural features. Of course a disadvantage of simulation is that the number of particles and the timescale of the simulation is limited by present day computing power. Recent algorithmic developments [*13-14*] have enabled us to make some inroads into the study of large-scale systems over longer time scales than any other studies, following the crystallisation path over many billions of hard sphere collisions.

2. SIMULATION OF HARD SPHERE CRYSTALLISATION.

Four systems of 12,000 spheres were used in our initial attempts to study hard sphere crystallisation. These spheres were set up in a cubic box (with periodic boundary

conditions), at a packing fraction of 0.3, initially in a lattice arrangement which was then allowed to melt to produce a fluid configuration. This configuration was slowly compressed isotropically to the reduced density $\rho^* = 1.1$ (packing fraction $\phi = 0.576$). At this density the pressure of the metastable pure hard sphere fluid is around 23.5 in reduced units of $\beta\sigma^3$ where σ is the hard sphere diameter and $\beta = 1/k_BT$. On completion of the densification at $\rho\sigma^3 = 1.1$ the pressure can exceed the metastable fluid branch value.

Figure 1. shows the relaxation of each of these systems over several million collisions. It appears that there is no barrier to spontaneous homogeneous nucleation as initial nucleation events appear throughout each system, made evident by the immediate and continuous drop in pressure in both systems down to a plateau region at a pressure of around 18 k_BT /σ^3. The early stages of crystallisation are independent of the starting configuration as the pressure in both systems falls in a very similar manner initially. In the intermediate regions where the pressure settles around 18 k_BT/σ^3 the evolution of each system follows a more spasmodic path – the number of collisions required to produce a substantial pressure drop varies in each system although eventually it can be seen that they both approach the same pressure, just above 15 k_BT/σ^3. The pressure of a pure fcc crystal at this packing fraction is 14.6 k_BT/σ^3.
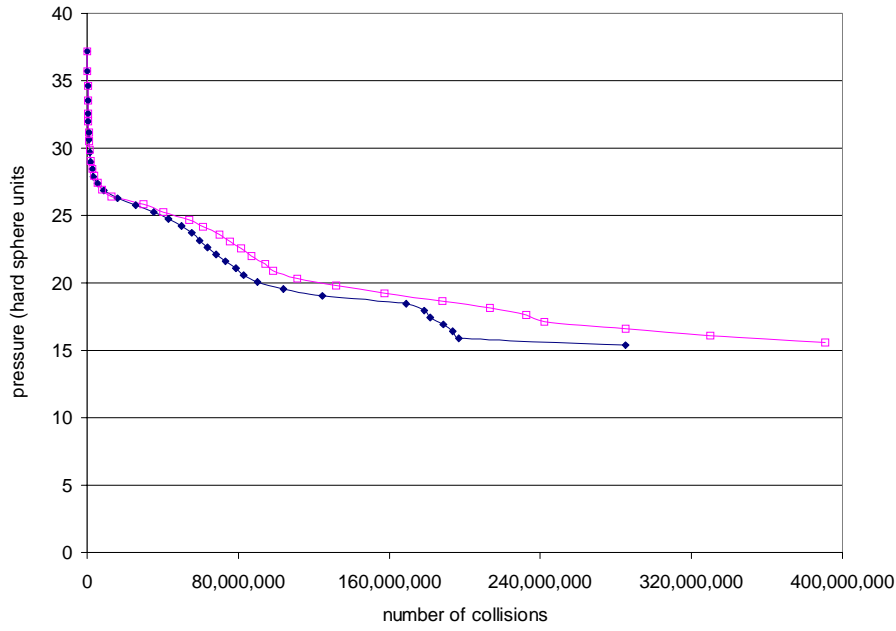
Figure 1. The evolution of pressure with number of collisions for two systems of 12,000 hard spheres)initially densified to a fluid state at a packing fraction of 0.576) as they crystallise.

More detailed information of the nucleation process and the evolution of crystal structures has been obtained from continual analysis of the transient and final configurations using angular order parameters *[15]* and modified Voronoi polyhedra *[16]*. We have calculated the bond-order parameter distributions wherein every atom in the system can first be distinguished as either crystalline or fluid using the method of ten Wolde et al. *[*17*]*. Subsequently, local fcc ordering can be distinguished using the heuristic established by Mitus et al. First, they calculated the local order parameter w_{446} for each particle in the system. The distribution of this parameter for a pure fcc crystal showed a distinct separation from other crystalline ordering. Using this approach we identified only those particles with a local order parameter lying within the pure hard sphere fcc crystal local order parameter distribution as fcc. Verification of such an identification was made by examining the modified Voronoi polyhedron surrounding each particle. Local hexagonal ordering and body centred cubic order could also be identified accurately using the Voronoi construction.
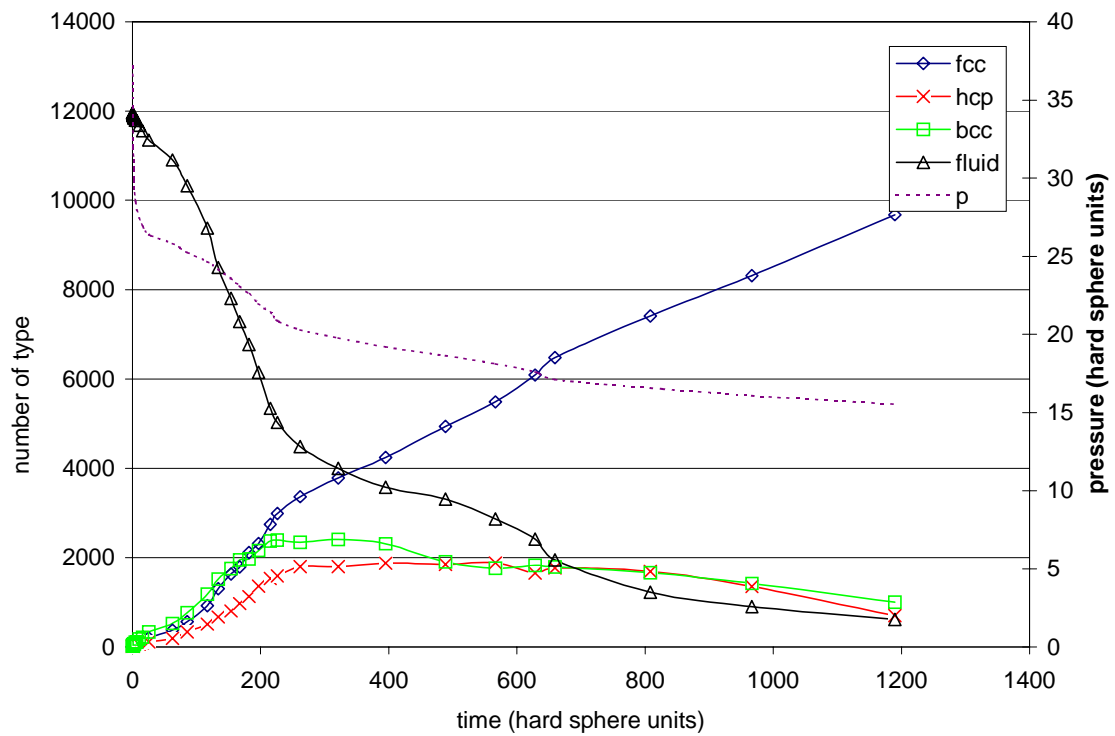
Figure 2 The evolution of structural content in a crystallising system of 12000 spheres.

With these techniques we observed (figure 2) that initially bcc, fcc, and hcp nucleites can all appear spontaneously out of local density fluctuations throughout the system simultaneously. The amount of sample that can characterised as "fluid" drops to around a quarter of the system after 500 hsu. At this stage nucleites are beginning to fill the system and the "fluid" is found at boundaries between nucleites. At this early stage the predominant structure is fcc. For the next 1000 hsu, in a long annealing phase, the fcc fraction grows, the bcc decays slowly; along with the rhcp content. The final structures in four independently prepared N=12000 systems were characterised by these methods to reveal the orderings shown in Figure 3.
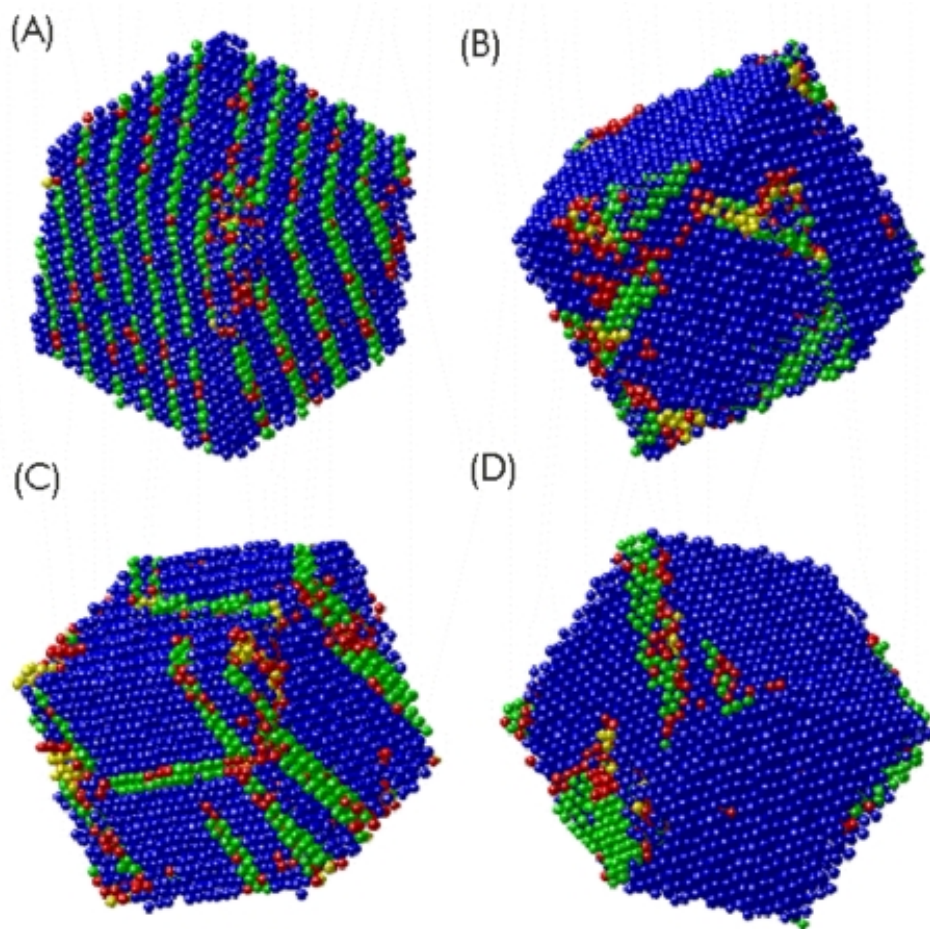
Figure 3 Kinetically stable structures that emerged in independently crystallized 12000 particle systems. Blue colouring of a sphere denotes local fcc order, green colouring hcp order, red bcc and yellow "fluid" content. (A) has a 65% fcc content, (B) has 81% fcc, (C) has 70% fcc while (D) has 82% local fcc content.

Clearly the annealing phase can lead to wildly varying final structures although it can be noted that in all the crystal structures the fcc content dominates at the end of this phase. An interesting observation was made from these crystallisations that may be a useful and fundamental generality. The structural identification as a function of time appears to vary widely from one run to the next because the crystallisation process is dependent on infrequent random events (perhaps extreme density fluctuations); the proportion of crystal type and the ratio of fluid to crystal at any point along the crystallisation path appears to depend only on the transient pressure of the system, as shown in Figure 4. Rather than discuss the system evolution with time it makes more sense to discuss the process of crystallisation as the pressure of the system decreases since this eliminates the differences between systems imposed by rare-event statistics.
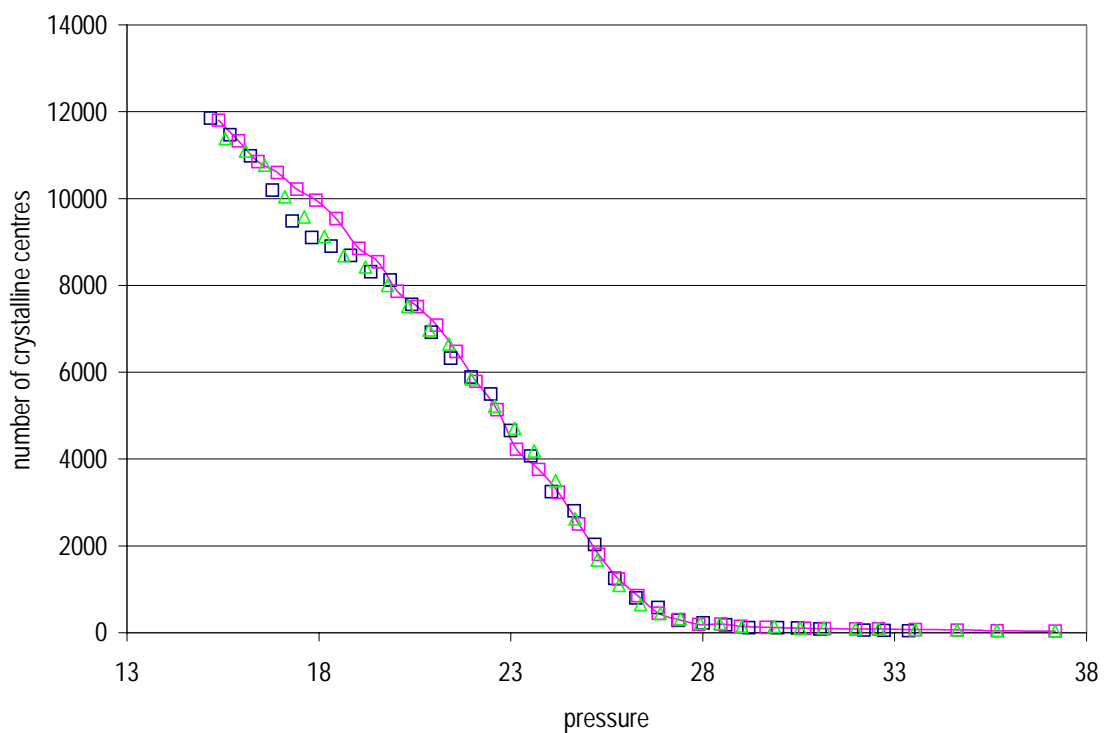

Figure 4 The amount of crystalline content plotted against the pressure (in hsu) for independently prepared systems of N=12,000 hard spheres with ϕ=0.576
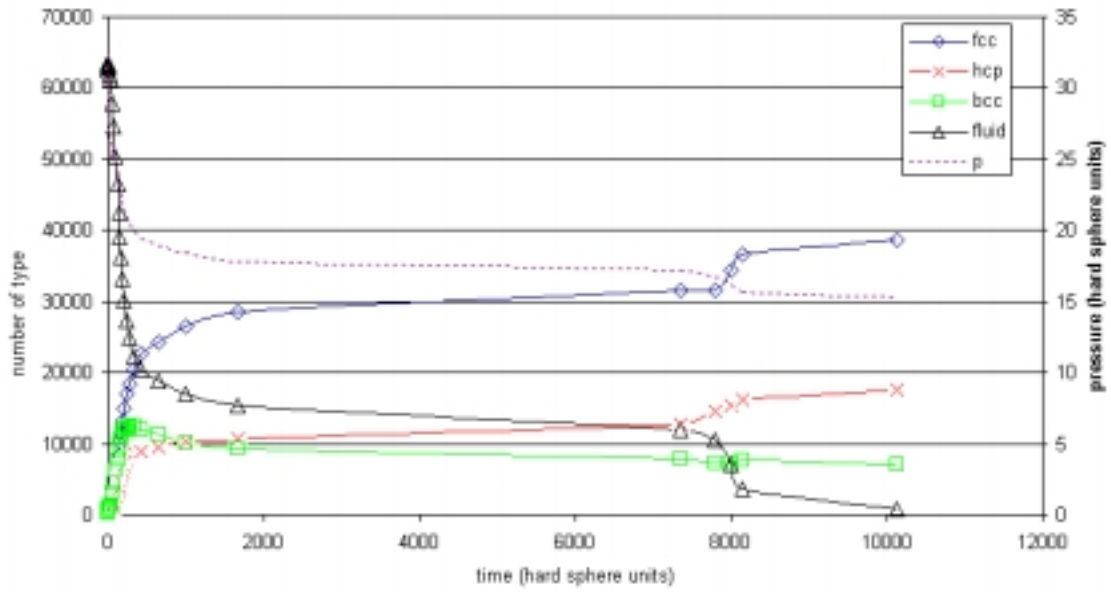
Figure 5 The emergence of fcc, bcc, hcp crystal structures from the metastable fluid with time (in hard sphere units) in an N=64000 particle system. The evolution of the system pressure with time is also plotted with the pressure scale on the right hand axis.

Whether or not this is a useful generality will depend upon whether the same observations can be made for crystallisation at differing packing fractions and differing system sizes. If the observation that the relative concentration of crystalline content is a function of only pressure it is tempting to project the crystallisation mechanism to larger systems such as those encountered in colloidal hard sphere experiments where the number density of particles can be around 10^{14} cm^{-3}. With the aim of looking at the system size dependence, a set of 64,000 hard spheres in a disordered arrangement was created with a packing fraction of 0.576 and allowed to crystallise. Here a slightly different picture emerges to that seen in the smaller system. At early stages we observe the same hand in hand growth of fcc and bcc content, followed by a depletion of bcc content alongside the steady growth of fcc and hcp content. However the behaviour of the larger system in the final stages of crystallisation differs substantially – at no point in this state does the hcp content become depleted. Figure 5 shows the variation in structural content with time and we note that there is apparently a system size dependence to the time taken in the annealing phase. The pressure drops rapidly to around 18 k_BT/σ^3 in around 400 hsu, along the same timescale as the smaller N=12,000

system. This is followed by an immensely longer annealing timescale that is suggestive of a more complex distribution of crystalline orientations in the system – an alignment and subsequent growth may require an improbable density fluctuation; if there are several alignments required to stimulate crystal growth then a substantially longer time will elapse before the larger system of particles becomes almost fully crystalline. After this long annealing process in the larger system taking the pressure down to around 17.2 k_BT/σ^3 a sharp drop in pressure occurs taking the system down to a pressure of 15.2 k_BT/σ^3, in the same manner observed in the smaller system. We present a series of snapshot images of the system as it undergoes this transition (Figure 6). They show, very clearly, that the system initally forms faulted fcc/hcp crystalline mixtures or "grains" (A) surrounded by disordered boundaries that are eventually eradicated (B) – (E) until finally a faulted and defective set of close packed layers (F) is produced as the pressure reaches a plateau.
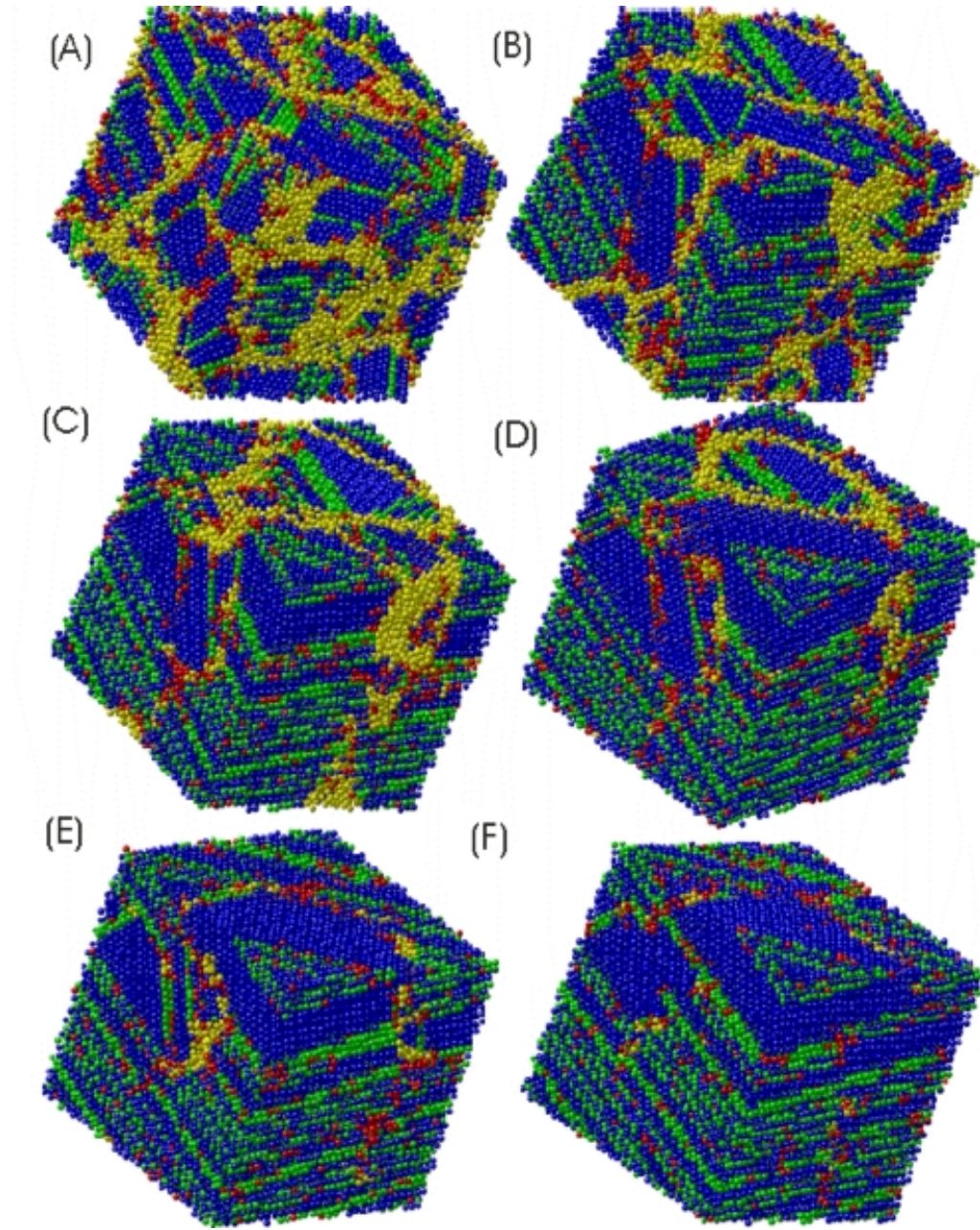
Figure 6. A series of snapshots from the system of 64,000 spheres in the annealing phase as the pressure drops from (A) 17.8 (B) 17.2 (C) 16.7 (D) 16.2 (E) 15.7 to (F) 15.2 k_BT/σ^3

In conclusion, we see observe that in the initial stages of freezing the metastable fluid generates small nuclei. From a thermodynamic viewpoint it is the chemical potential difference between the fluid and crystal phases that is the essential driving force for this. With this perspective we know from recent theory that the bulk face centred cubic structure is the most stable crystal structure and so we might expect the fcc crystal

phase to dominate. However nuclei growth kinetics are governed by surface free energy factors competing with the bulk free energy differences. Our simulation evidence suggests that the emergence of crystal structures from the fluid follows Ostwald's step rule which anticipates the influence of surface free energy factors. Ostwald formulated the rule that the crystal phase nucleated from the fluid could in fact be the one that is nearest in free energy to the fluid phase rather than the one furthest away (i.e the most stable). In these simulations we see, initially, the growth of bcc and fcc structural components with bcc leading fcc slightly. Woodcock [18] found that the bcc lattice melts at a packing fraction of 0.548 and begins to freeze at a packing fraction of 0.528, with a coexistence pressure slightly higher than the fcc-fluid coexistence pressure. The operation of Ostwald's step rule, with the bcc phase predominating among the earliest nuclei, at a packing fraction of 0.576 is feasible given this evidence.

At early stages the appearance of fcc structural content is also rapid, travelling almost hand in hand with the bcc growth. Although this could be attributed to the thermodynamic drive to achieve the state with the lowest free energy, it may also be due to an inherent coupling of the unconstrained hard sphere bcc crystal with the fcc crystal. We have observed that a bcc lattice of 16000 hard spheres is unstable at a packing fraction of 0.576, rapidly losing its structural integrity to collapse to a faulted mixture of fcc and hcp structures. Local fluctuations and resulting stresses are capable of inducing slip in the bcc lattice. The mechanical instability of the bcc crystal thus presents a plausible mechanism for the coupling of fcc and bcc nuclei growth.

At intermediate stages the crystallisation has a percolative character where crystalline regions containing many variations of local order, intermingled, and spanning the whole system. A slow conversion and growth of nuclei occurs at this stage with large regions gradually reducing the local bcc content to form predominantly fcc structures albeit containing numerous stacking faults. At later stages annealing of nuclei in the system can occur provoking more stacking faults and the crystallisation follows an unpredictable path, once seemingly kinetically stable structures are obtained. It is observed that from simulation to simulation these vary from having almost all fcc content to being completely rhcp, and in some cases mixtures. This result is entirely consistent with the stable crystal structure of hard-spheres in the thermodynamic limit being essentially 50% fcc and 50% rhcp in accord with the different symmetry and free energy difference of 0.001kT.

This essentially random outcome seems to be independent of the size of the system that is studied. The present computations confirm neither complete crystallisation to either fcc or rhcp. Experiments on colloids under the influence of gravity suggest a long time scale for crystallisation towards a wholly fcc structuring. On the other hand, the experiment undertaken in microgravity describe stable rhcp structures appearing on a much shorter time scale. However the claim for "rhcp" in this experiment requires closer examination. The existence of rhcp structuring was deduced from the absence of an fcc signature peak in the scattered intensity from the sample. In these simulation studies we also find an absence of the fcc signature peak at

intermediate and annealing timescales. It may simply be that the microgravity experiments represent unstable hard-sphere systems which are in this slow grain growth conversion process.

Very recent work by Pronk and Frenkel *[19]* also suggests that this is the case and goes some way to explaining the unpredictable latter stage of crystallisation in our simulated systems. Pronk and Frenkel remark that is "unsurprising" that the microgravity experiments of Zhu et al. (duration: two weeks) showed only rhcp crystallites, estimating that "it would take several months to grow a 1mm fcc crystal". Additionally in these small system sizes we cannot attain a rich distribution of crystalline grains – we can manage two or three small grains at most. The evolution of the system in these latter stages is dominated by the characteristics of these grains.

---

1 "Measurement of the hard sphere equation of state using screened charged polystyrene colloids" Rutgers M.A., Dunsmuir J.H., Xue J-Z., Russel W.B. and Chaikin P.M. Phys. Rev. B. **53** pp. 5043 – 5046 (1996).

2 "Evidence of FCC crystallisation of SiO2 nanospheres" Miguez H., Meseguer F., Lopez C., Mifsud A., Moya J.S. and Vazquez, L., Langmuir **13** No.23, pp. 6009 – 6011 (1997)

3 "Colloids make ultrafast optical devices" Grier D., Physics World, July, pp 24 – 25 (1997).

4 "Template-directed colloidal crystallisation" van Blaaderen A., Ruel R. and Wiltzius P., Nature **385** pp. 321 – 324 (1997).

5 "Opals in a new light" van Blaaderen A., Science **282** pp. 887 – 888 (1998).

6 "Structure of crystals of hard colloidal spheres" Pusey P.N., van Megen W., Bartlett P., Ackerson B.J., Rarity J.G. and Underwood S.M., Phys. Rev. Lett. **63** No. 25 pp. 2753 – 2756 (1989)

7 Stacking probabilities of 0, 0.5, and 1 correspond to the hcp, random hexagonally layered close packing (rhcp) and fcc structures respectively.

8 *"Direct measurement of stacking disorder in hard-sphere colloidal crystals"* Elliot M.S., Bristol B.T.F. and Poon W.C.K., Physica A **235** pp. 216 – 223 (1997).

9 *"Light diffraction from shear ordered colloidal dispersions"* Dux C. and Versmold H., Phys. Rev. Lett, **78** No.9 pp. 1811 – 1814 (1997)

10 *"Observation of oriented close packed lattice planes in polycrystalline hard sphere solids"* Heymann A., Stipp A., Sinn C. and Palberg T., J. Coll. Int. Sci. **207** pp. 119 – 127 (1998).

11 *"Wetting state of a crystal-fluid system of hard spheres"* Courtemanche D. J. and van Swol F., Phys. Rev.Lett. **69** No.14 pp. 2078 – 2081 (1992)

12 *"Crystallisation of hard sphere colloids in microgravity"* Zhu J., Min L., Rogers R., Meyer W., Ottewill R., STS-73 Space Shuttle Crew, Russel W.B. and Chalkin P.M, Nature, **287** pp. 883 – 885 (1997)

13 *"How to simulate billiards and similar systems"* Lubachevsky B.D., J. Comp. Phys., **94** pp. 253 – 283 (1991)

14 *"Efficient algorithms for many-body hard particle molecular dynamics"* Marin M., Risso D. and Cordero P., J. Comp. Phys. 109 pp. 306 – 317 (1993)

15 *"Bond orientational order in liquids and glasses*" Steinhardt, P.J., Nelson, D.R. and Ronchetti, M., Phys. Rev. B. **28** No.2 pp. 784 – 805 (1983).

16 *"Voronoi polyhedra and Delaunay simplexes in the structural analysis of molecular dynamics simulated materials"* Brostow, W., Chybicki, M., Laskowski, R. and Rybicki, J., Phys. Rev. B. **57** No.21 pp. 13448 – 13458.

17 *"Numerical calculation of the rate of crystal nucleation in a Lennard-Jones system at moderate undercooling"* ten Wolde, P.R., Ruiz-Montero, M. J. and Frenkel, D., J. Chem.Phys. 104 No.24 pp. 9932 – 9947 (1996).

18 ***"Computation of the free energy fir alternative crystal structures of hard spheres"*** Woodcock, L.V., Faraday Discuss. 106 pp. 325 – 338 (1997)

19 *"Can stacking faults in hard-sphere crystals anneal out spontaneously?"* Pronk, S. and Frenkel, D., J.Chem.Phys. **110** No. 9. pp. 4589 – 4592 (1999).